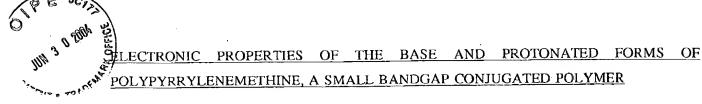
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## **ABSTRACT**

We present MNDO geometry optimization results and VEH band structure calculations on the base and protonated forms of polypyrrylenemethine (PPM), a conjugated polymer based on oxidized pyrrole rings bridged by a methine-type carbon.

The 1.47 eV bandgap calculated for neutral PPM decreases to 0.78 eV after protonation of the nitrogens. This is a consequence of the geometry modifications imposed by the protonation process which leads to a situation where the pyrrole rings alternate between aromatic and quinoid geometries. It is important pointing out that both the neutral and protonated forms of PPM have been recently synthesized.

## INTRODUCTION

The recent synthesis of PPM through a condensation reaction on pyrrole-2-carbaldehyde represents a significant advance in the field of conjugated polymers that possess small intrinsic bandgaps [1,2]. This polymer can be obtained as a powder, coating, or film, and exhibits a bandgap of  $\approx 1$  eV [1,2]. After polymerization, all the nitrogens atoms of PPM are found to be protonated. Extraction with NH<sub>3</sub> then produces the base form of the polymer. However, the maximum number of deprotonated nitrogens amounts to about 30%.

In this contribution, we present MNDO (Modified Neglect of Differential Overlap) [3] geometry optimizations and VEH (Valence Effective Hamiltonian) [4] band structure calculations on both the neutral and protonated forms of PPM.

#### **NEUTRAL PPM**

The unit-cell of neutral PPM is depicted in Figure 1, as obtained after a MNDO geometry optimization on a four-ring oligomer. All C-C and C-H bond lengths and all bond angles are optimized in a coplanar conformation.

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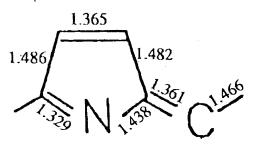
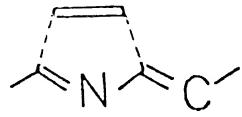


Figure 1. Geometric structure of neutral PPM. Bond lengths are given in Å and angles in degrees. The system is assumed to be planar.

The VEH electronic properties of neutral PPM are given in TABLE I, together with those of the neutral PPM conjugated <u>backbone</u> and fully protonated PPM. For the sake of comparison, the electronic parameters of polyacetylene and polymethineimine are also provided. The bandgap calculated for neutral PPM is 1.47 eV, i.e. a value twice smaller than that of (aromatic) polypyrrole. The magnitude of this bandgap can be easily rationalized if one considers the polymeric chain as being composed of a carbon-nitrogen conjugated backbone in interaction with ethylenic units:



First, the electronic properties calculated for the neutral PPM backbone are representative of what usually takes place in copolymers, i.e. they are intermediate between those of the parent polymers (in this case, polyacetylene and polymethineimine). Then, the interaction between the wavefunction of the conjugated backbone and the wavefunction of the ethylenic units within the pyrrole rings induces a stabilization of the backbone LUMO (Lowest Unoccupied Molecular Orbital) to produce a gap of 1.47 eV in neutral PPM. Unfortunately, no optical absorption measurements on the neutral form of PPM have been reported until now.

TABLE I VEH values of ionization potential (IP), electron affinity (EA), highest occupied band width (HOBW), and bandgap (Eg) for neutral PPM, neutral PPM backbone, polyacetylene (PA), polymethineimine (PMI), and protonated PPM. All values are given in eV.

	IP	EA	HOBW	Eg
neutral PPM	6.01	4.54	1.59	1.47
backbone	6.08	2.27	2.72	3.81
PA* <sup>)</sup>	4.76	3.32	6.50	1.44
PMI <sup>a)</sup>	8.28	2.10	3.52	6.18
protonated PPM	5.88	5.10	1.54	0.78

a) from Ref. 4.

# PROTONATED PPM

The protonated PPM unit-cell was obtained after a MNDO geometry optimization on a four ring oligomer where two protons were added on the central rings. The geometric structure is given in Figure 2.

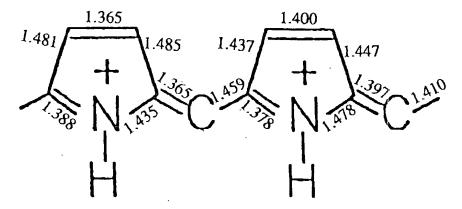


Figure 2. Geometric structure of protonated PPM. Bond lengths are given in Å and angles in degrees. The system is assumed to be planar.

The addition of protons on the imine nitrogens of an oxidized polypyrrole chain induces strong geometry modifications. These tend to equalize the carbon-nitrogen bond lengths along the conjugated backbone within the two rings (the single C-N bonds slightly shorten from 1.438 Å to 1.428 Å and 1.435 Å while the double bonds significantly elongate from 1.329 Å up to 1.378 Å and 1.388 Å). The situation occurring between the rings is quite different: one bridging unit is not affected by the protonation while the other undergoes strong geometry modifications by which the single bond shortens from 1.466 Å to 1.410 Å and the double bond elongates from 1.361 Å to 1.397 Å.

A similar evolution appears inside the pyrrole rings: the nitrogen protonation has no effect on the geometry of one ring where  $\alpha$ - $\beta$  and  $\alpha$ - $\beta$  bond lengths are equal to 1.485 Å and 1.365 Å, respectively, as in the unprotonated case. In the other ring, however, the  $\alpha$ - $\beta$  bond lengths shorten from 1.482 Å to 1.447 Å and from 1.486 Å to 1.437 Å while the ethylenic unit length elongates up to 1.400 Å.

All these geometry modifications do totally change the polymer geometric structure. The chains are no longer composed of oxidized pyrrole rings separated by a methine-type carbon (case of neutral PPM) but rather of pyrrole rings alternating between aromatic and quinoid geometries and bridged by a methine-type carbon (Figure 3). This is in perfect agreement with the interpretation of the experimental data [2]. It is most interesting to note that an MNDO geometry optimization on a polybipyrrolemethenylene chain (where alternating aromatic and quinoid pyrrole rings are separated by a conjugated carbon) from which two electrons are extracted, has given identical results [5].

The strong electron-lattice coupling existing in conjugated polymer makes that those geometry changes are reflected in the electronic structure of protonated PPM. The bandgap is calculated to be 0.78 eV, i.e. a value twice smaller than that of neutral PPM. This low bandgap for protonated PPM is in very good agreement with optical absorption measurements (the onset of the absorption lies at 0.8 eV) [1,2] and the conclusions of an earlier theoretical study on the electronic structure of neutral polybipyrrolemethenylene [6].

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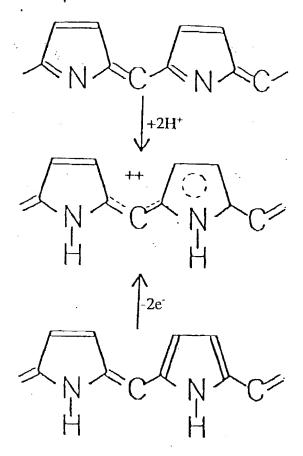


Figure 3. Evolution of the geometry when two protons are added on a neutral PPM chain and when two electrons are extracted from a polybipyrrolemethenylene chain.

# **ACKNOWLEDGEMENTS**

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